THE DETERMINATION OF THE DISSOCIATION CONSTANT OF MONOCHLOROACETIC ACID IN SOLVENTS OF VARIOUS DIELECTRIC CONSTANTS BY CONDUCTANCE MEASUREMENTS

A THESIS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

During the reign of the Arrhenius theory of electrolytic dissociation, an electrolyte was classified as being strong or weak according to the conductivity of its aqueous solutions. While this method of classification presented a convenient working rule, thinking in such terms very probably contributed to the prolonged concealment of the important concept of ionic mobilities. The conductance of a solution is dependent upon the mobility of the ions as well as the number of ions in the solution. It is clear that the mobility of the ions of a given solute in a medium are dependent upon the nature of the medium. Thus a so-called strong electrolyte may exhibit low or high conductivity depending upon the medium in which it is dissolved.[1]

According to the ion-atmosphere theory of Debye-Huckel-Onsager, the two solvent properties which contribute most to the conductivity of a solution are the viscosity and the dielectric constant.[2] The first systematic study of the effect of the dielectric constant of the medium upon the conductance of solutions of electrolytes was made by Kraus and Fuoss beginning in 1933.[3,4,5] As solvents they used dioxane (D = 2.2), benzene (D = 2.8), ethylene dichloride (D = 10.4), water (D = 78.6) and mixtures of these liquids. They observed no effects of solvent upon conductance with the exception of the effects produced by differences in viscosity or differences in dielectric constants. However, it was noted that in solvents of very low dielectric constant (D = less than 10) a minimum

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[1] N. F. Hall & H. H. Voge, J. Am. Chem. Soc., 55, 239 (1933).
[2] P. Debye & L. Onsager, Trans. Far. Soc., 23, 341 (1927).
[3] C. A. Kraus & R. M. Fuoss, J. Am. Chem. Soc., 55, 21 (1933).
[4] Ibid., p. 476.
[5] Ibid., p. 1019.

occurred in plots of the conductance data, the slopes of the plots were greater than the theoretical slopes as given by the Onsager equation and the curves were quite complex in the regions corresponding to the higher concentrations.

The first attempt to explain the various anomalies of this type was a proposal by Bjerrum.[6,7] He postulated that when ions of opposite charge approach each other within a certain distance, they may unite to form an ion-pair which does not conduct the current. Fuoss and Kraus [8,9] combined this idea with the Onsager equation and the Debye-Huckel expression for the activity coefficient to the interpretation of conductance data and arrived at a method of graphical extrapolation by which they successfully determined the limiting conductance for a number of electrolytes. They attributed the high value of the slopes to the formation of ion-pairs. From the standpoint of interionic, attraction, this should be expected in solvents of very low dielectric constant. [10] The appearance of the minimum in the conductance curve was ascribed to the formation of triple ions [11, 12] and the inflection points appearing in the regions of higher concentrations to the formation of clusters of more than three ions. [13,14,15]

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[6] N. Bjerrum, Ber., 62, 1091 (1929).
[7] A. Davidson, J. Chem. Ed., 14, 224 (1937).
[8] R. M. Fuoss & C. A. Kraus, J. Am. Chem. Soc., 55, 476 (1933).
[9] Ibid., p. 1019
[10] R. M. Fuoss, Chem. Rev., 17, 27 (1935).
[11] A. Davidson, op. cit.
[12] R. M. Fuoss & C. A. Kraus, J. Am. Chem. Soc., 55, 2387 (1935).
[13] R. M. Fuoss & C. A. Kraus, op. cit., 3614 (1933).
[14] C. B. Wooster, J. Am. Chem. Soc., 60, 1609 (1938).
[15] C. A. Kraus, J. Chem. Ed., 12, 570 (1935).

The extrapolation method of Kraus and Fuoss, though successful, was quite laborious. In a later paper,[16] Fuoss introduced a simpler method which he showed to be applicable to solutions whose concentrations did not exceed $3.2 \times 10^{-7}\ D^3$ at 25°C. for uni-univalent electrolytes. Kilpatrick[17] made a study of the possible error in the extrapolation of conductance data of weak acids and concluded that reliable results could be obtained for acids whose dissociation constants were greater than 10^{-3}. Noting that the method of Fuoss required the use of a table which might not always be available, Shedlovsky[18] introduced a method which appears to give results equally as good or better than that of Fuoss without the use of a table.

The present investigation was undertaken in order to obtain conductance data for the behavior of a moderately weak electrolyte ($K = 2 \times 10^{-3}$, approximately) in media of different dielectric constants with the aim of applying the methods of Kraus and Fuoss for the interpretation of these data. Since dioxane is completely miscible with water, it was chosen as the solvent of low dielectric constant and water as the solvent of high dielectric constant. Solvents having dielectric constants of intermediate values were conveniently prepared using various mixtures of these two liquids. Thus it is possible to obtain data over a dielectric constant range from 2.2 to 78.54.

The electrolyte chosen for study was monochloroacetic acid. It was previously studied in aqueous solution by several workers.[19] We were unable to find data regarding its behavior in non-aqueous media.

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[16] R. M. Fuoss, J. Am. Chem. Soc., 57, 488 (1933).

[17] M. L. Kilpatrick, J. Chem. Phys., 8, 306 (1940).

[18] T. Shedlovsky, J. Frank. Inst., 225, 739 (1938).

[19] B. S. Saxton & T. W. Larger, J. Am. Chem. Soc., 55, 3638 (1933).

MATERIALS AND APPARATUS

The dioxane was purified according to the method of Vingee.[20] Crude dioxane was refluxed for three hours with solid sodium hydroxide. The liquid was decanted and dried overnight over barium oxide. The product was then refluxed over metallic sodium for two hours and finally fractionally distilled. The boiling point of the pure compound was 99°C. at 732 millimeters of mercury.

Conductance water was prepared by redistilling distilled water to which had been added a little potassium permanganate and sodium hydroxide. The receiver was a 500 ml. flask having a side-arm connected to a flask containing concentrated sulfuric acid and subsequently to a drying tube containing soda lime. These precautions were taken in order to keep out the carbon dioxide and ammonia present in the atmosphere. The water was condensed at a relatively high temperature as a further precaution. The whole apparatus with the exception of the acid trap and the absorption tube was steamed out prior to collecting the water. The water was stored in Pyrex flasks with ground-glass stoppers at first. However, it was noticed that the conductance of the water increased on standing and it was decided to use freshly distilled water throughout the experiment. The conductance of the water so obtained was 2.1×10^{-5}.

Baker's "Analyzed" monochloroacetic acid was distilled twice at 0.5 mm pressure, the first fraction (77-80°C.) being discarded in each case. The purified product was a white crystalline solid melting at 62°C. which gave no immediate precipitate or cloudiness with silver nitrate solution.

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[20] C. A. Kraus & R. M. Fuoss, J. Am. Chem. Soc., 55, 21 (1933).

The potassium chloride used for cell constant determination was taken directly from stock being of a good grade. The bridge used was of the Shedlovsky type[21] modified by Edelson and Fuoss[22] with minor alterations made in this laboratory. A Jackson #655 continuously variable oscillator was used, eliminating the necessity for the frequency selector switches. The bridge proper was a L. & N. #1553 Campbell-Shackelton ratio box which contained the matched ratio arms, the Wagner grounding device[23] and a shielded input transformer. The unit was built into the bridge with one alteration: the slide-wire in series with the resistor across $S1^{+} - S1^{-}$ was put in parallel with this resistor. The amplifier was built with one alteration: the R-C circuit in the third and final stage was eliminated. The resistance box used was a General Radio shielded decade box variable from 1 to 111,110 ohms. As a balance instrument, a Hickok Model 670 oscillograph was used. The method of balance used was the same as outlined in the original article.[24]

For solutions of high resistance, it was necessary to connect a high resistance shunt from A to ground and for solutions of low resistance, it was necessary to insert a variable air capacitor across the decade box.

All measurements were made at 25° C. Temperature control was effected by means of a ten gallon thermostat in which water was used as a cooling medium. The temperature of the bath remained constant during measurements within $\pm$ 0.01° C.

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[21] T. Shedlovsky, J. Am. Chem. Soc., 52, 1793 (1930).
[22] D. Edelson & R. M. Fuoss, J. Chem. Ed., 27, 610 (1950).
[23] Op. cit.
[24] Op. cit.

The cell used was of the Washburn type designed for use with water or very dilute solutions. The cell constant was determined through the use of 10^{-3} and 10^{-4} normal aqueous potassium chloride solutions and averaging the results. The molecular weight of potassium chloride was taken as 74.59 as suggested by Kohlrausch and Holburn[25] and the values for the equivalent conductances of the potassium chloride solutions were those suggested by Daniels and staff.[26] The resulting values, shown in Table I, though not exact,[27] were sufficiently accurate for this work.

TABLE I

DATA FOR DETERMINATION OF CELL CONSTANT

0.001 N	3.676×10^{-3}	2.09×10^{-5}	273.9	0.04022
0.0001 N	3.843×10^{-4}	2.09×10^{-5}	2751.9	0.04098
			(average)	0.04060

[25] G. Jones & B. S. Bradshaw, J. Am. Chem. Soc., 55, 1794 (1933).

[26] F. Daniels, "Outlines of Physical Chemistry," John Wiley & Sons, Inc., New York, 1948, p. 403.

[27] Op. cit.

PROCEDURE

Considerable difficulty was experienced in determining the cell constant, presumably because of some peculiarity of the cell itself. A comprehensive study of cell design has been made by Jones and his co-workers.[28,29] For a design suited to very precise work, the reader is advised to consult these papers. In our work, it was found that unplatinized electrodes gave fairly consistent results, thus they were used throughout the determination. Jones and Bollinger[30] observed that polarization is minimized by platinization in general, but stated that platinization should be minimized or eliminated when working in acidic, basic or very dilute solutions. It should be stated here that it is quite possible that, in our work, difficulties with the cell presented a constant source of error.

Approximately tenth-normal solutions of monochloroacetic acid were prepared using various mixtures of water and dioxane as solvents. The solvents chosen for study were, in terms of dioxane by weight, 100%, 80%, 50%, 20% and 0%. The procedure used was as follows.

Fifty milliliters of an approximately tenth-normal solution of monochloroacetic acid was pipetted into the cell. The arms of the cell were then closed using Tygon tubing and the cell was immersed in the constant temperature bath where it remained for thirty minutes before a reading was taken. After the resistance of the solution was measured, the cell was carefully dried and its contents emptied into a 125 milliliter flask. Twenty-five milliliters of this solution were then pipetted into a 100 milliliter

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[28] G. Jones & B. S. Bradshaw, loc. cit.
[29] G. Jones & D. Bollinger, J. Am. Chem. Soc., 53, 1207 (1931).
[30] G. Jones & D. Bollinger, J. Am. Chem. Soc., 57, 280 (1935).

volumetric flask and diluted to 100 milliliters. The cell was rinsed four times with twenty-five milliliter portions of the solvent and twice with the solution from the volumetric flask. Fifty milliliters of this solution were then added to the cell and another reading taken. In this manner, solutions were prepared whose concentrations ranged from 10^{-1} to 10^{-6} normal approximately.

Due to the hygroscopic nature of the chloroacetic acid, the initial concentrations were determined by preparing solutions approximately tenth-normal and titrating with sodium carbonate solution to determine exact normalities. The titrations were done potentiometrically for more precise results. The concentrations of each solution used in the determination are tabulated in Table II.

TABLE II

CONCENTRATIONS OF ACID IN INDIVIDUAL SOLUTIONS

Soln. No.	80% Dioxane	50% Dioxane	20% Dioxane	Water
1	1.01×10^{-1}	1.03×10^{-1}	1.01×10^{-1}	9.60×10^{-2}
2	2.53×10^{-2}	2.58×10^{-2}	2.53×10^{-2}	2.40×10^{-2}
3	6.32×10^{-3}	6.45×10^{-3}	6.32×10^{-3}	6.00×10^{-3}
4		1.61×10^{-3}	1.58×10^{-3}	1.50×10^{-3}
5		4.02×10^{-4}	3.95×10^{-4}	3.75×10^{-4}
6		1.00×10^{-4}	9.88×10^{-5}	9.40×10^{-5}
7			2.47×10^{-5}	2.30×10^{-5}
8			6.18×10^{-6}	5.80×10^{-6}
9			1.55×10^{-6}	1.45×10^{-6}

The resistance of the tenth-normal solution of chloroacetic acid in 100% dioxane was too high to be measured using our bridge, thus no data

is included regarding this solvent. Also, only three measurements could be taken using the 80% dioxane-water solution because of the high resistance of solutions of lower concentrations. An attempt was made to insert a fixed resistor in parallel to the cell in order that higher resistances of the solutions might be calculated but the results were unsatisfactory.

Jones and Christian[31] found that resistance decreases with increasing frequency and if the measured resistance is plotted against the square root of the frequency, the R intercept should be the actual resistance of the cell. In our work it was found that there was no consistent variation of resistance with frequency and it was decided to base all measurements on one frequency, namely 1000 cycles per second. Measurements were made at other frequencies, however, and the results are shown in Tables III-VI.

TABLE III

MEASURED RESISTANCES OF 80% DIOXANE SOLUTIONS

$f^{-\frac{1}{2}} \times 10^{2}$	#1	#2	#3
3.162	52980	60470	75400
2.887	52080	59700	74600
2.582	50800	59000	73550
2.236	48900	57500	72050
2.000	47500	56400	71100
1.826	46400	55300	70500
1.581	45000	53800	69600

[31] G. Jones & S. M. Christian, J. Am. Chem. Soc., 57, 272 (1935).

TABLE IV

MEASURED RESISTANCES OF WATER SOLUTIONS

$f^{-\frac{1}{2}} \times 10^{\frac{1}{2}}$	#1	#2	#3	#4	#5	#6	#7	#8	#9
4.472	10.00	17.22	40.80	114.4	340.1	1246	6896	20232	30619
3.546	10.00	17.82	40.83	114.4	339.8	1247	6896	20243	30640
3.162	10.00	17.82	40.83	114.4	339.9	1248	6896	20252	30644
2.887	10.00	17.60	40.80	114.3	339.8	1247	6896	20268	30660

TABLE V

MEASURED RESISTANCES OF 20% DIOXANE SOLUTIONS

$f^{-\frac{1}{2}} \times 10^{-2}$	#1	#2	#3	#4	#5	#6	#7	#8	#9
3.162	25.75	64.50	111.2	229.1	595.2	1887	7069	25960	34230
2.887	25.70	64.50	111.2	229.1	595.2	1887	7069	25960	34230
2.582	25.63	64.50	111.2	228.9	595.1	1889	7069	25960	34230
2.236	25.60	64.35	111.2	228.8	595.0	1890	7069	25960	34230
2.000	25.60	64.25	111.2	228.7	595.0	1890	7069	25960	34230
1.826	25.50	64.20	111.2	228.7	595.0	1890	7069	25960	34230
1.581	25.70	64.30	111.2	228.7	595.0	1890	7069	25960	34230

TABLE VI

MEASURED RESISTANCES OF 50% DIOXANE SOLUTIONS

$f^{-\frac{1}{2}} \times 10^{-2}$	#1	#2	#3	#4	#5	#6
3.162	168.2	371.8	771.2	1646	3650	9571
2.887	168.1	371.8	771.0	1646	3650	9506
2.582	168.1	371.7	770.9	1647	3650	9419
2.236	168.2	371.0	770.6	1646	3650	9296
2.000	168.4	371.1	770.5	1647	3649	9211
1.826	168.4	371.2	770.5	1647	3649	9152
1.581	168.5	371.2	770.3	1647	3649	9071

The viscosities of the dioxane-water solutions were obtained by graphical interpolation using data from the literature.[32] The graph is shown in Figure 1. The dielectric constants were determined according to the method of Akerlof using his tables.[33] The resulting viscosities and dielectric constants together with the resistances of the solvents are shown in Table VII.

TABLE VII

VISCOSITIES, DIELECTRIC CONSTANTS AND RESISTANCES OF THE SOLVENTS

	80%	50%	20%	Water
R		103060	56930	47880
	1.770	1.926	1.292	0.8937
D	10.71	34.32	60.82	78.54

[32] H. S. Harned & B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Co., New York, 1950.

[33] G. Akerlof & O. Short, J. Am. Chem. Soc., 58, 1241 (1936).

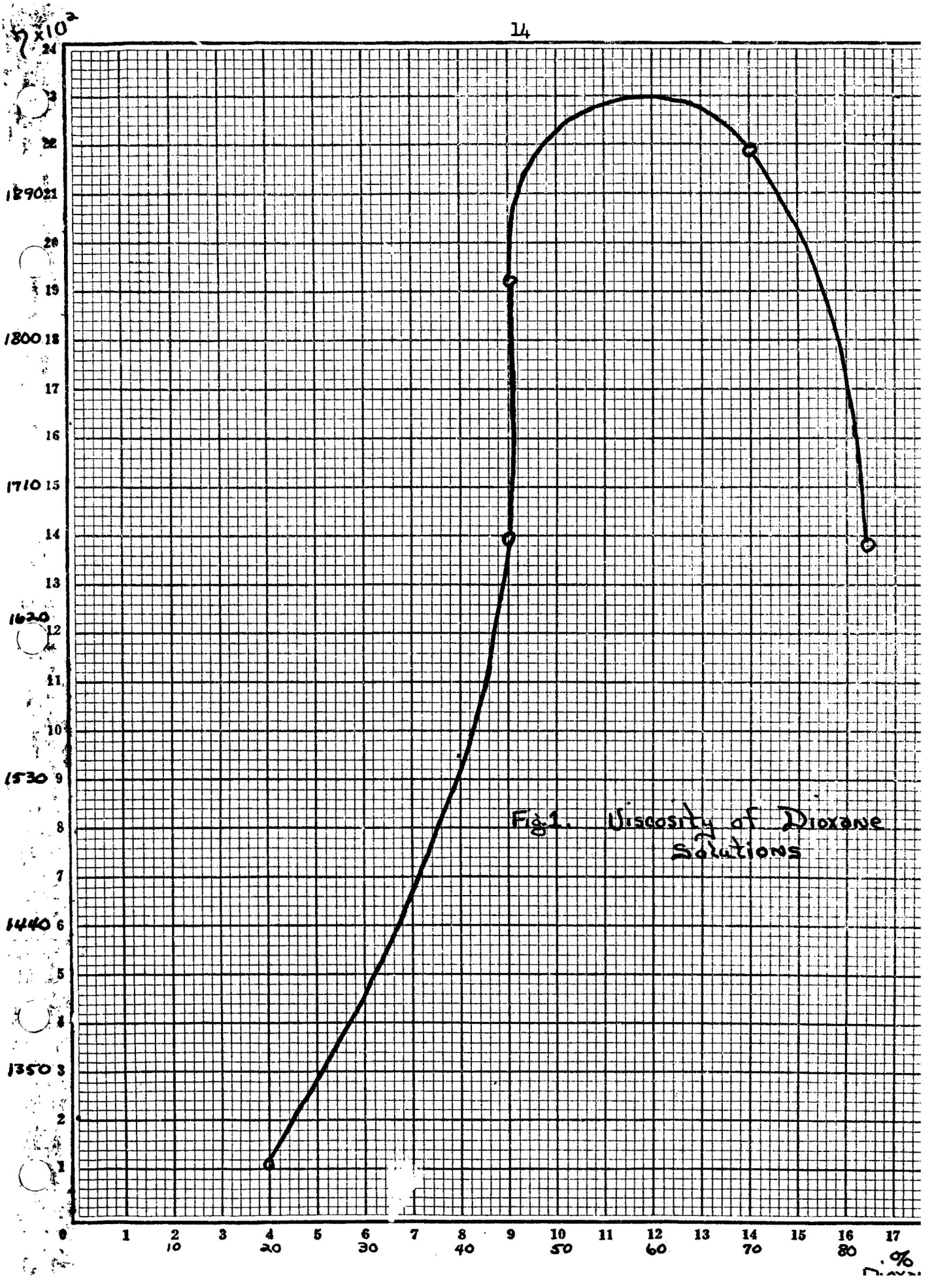

Fig. 1. Viscosity of Dioxane Solutions

EXPERIMENTAL RESULTS

Using the Kohlrausch square root law,

$$\Lambda = \Lambda^\circ - A\sqrt{c} \tag{1}$$

where Λ is the equivalent conductance, Λ° is the limiting conductance and c is the molar concentration, Onsager computed the constant, A, as being

$$A = S_\Lambda = \alpha^* \Lambda^\circ + \beta^* \tag{2}$$

For a uni-univalent electrolyte, α^* and β^* are dependent upon the solvent and temperature according to the following relations

$$\alpha^* = \frac{158.63}{D^{3/2}} \quad , \quad \beta^* = \frac{4.7483}{\eta D^{1/2}} \tag{3}$$

where D and η are the dielectric constant and the viscosity, respectively, of the pure solvent. According to Fuoss, the degree of dissociation, α, is expressed by the relations:

$$\alpha = \frac{\Lambda}{\Lambda^\circ F(z)} \tag{4}$$

where z is a correction factor computed from:

$$z = \frac{S_\Lambda}{(\Lambda^\circ)^{3/2}} \sqrt{c\Lambda} \tag{5}$$

and F(z) may either be determined from:

$$F(z) = 1 - z(1 - z(1 - z \ldots\ldots - \tfrac{1}{2})^{-\frac{1}{2}})^{-\frac{1}{2}} \tag{6}$$

or from a table compiled by Fuoss.[34]

When equations (1)-(6) are combined with the mass-law expression for the dissociation constant, the expression

$$\frac{F(z)}{\Lambda} = \frac{1}{\Lambda^\circ} + \frac{c\Lambda(y_\pm)^2}{K(\Lambda^\circ)^2 F(z)} \tag{7}$$

is obtained, where the activity coefficient, $(y_\pm)$, may be computed from:

$$\log y_\pm = 352.7\sqrt{\alpha c}\, D^{-3/2}.$$

[34] R. M. Fuoss, J. Am. Chem. Soc., 57, 488 (1935).

The method used in the determination of K is as follows: A trial value of Λ^0 is determined by plotting Λ vs $\sqrt{c}$ where Λ^0 is taken as the intercept on the Λ axis. Using this value, the other terms of equation (7) are determined and a plot of $F(z)/\Lambda$ vs $c\,\Lambda\,(y\pm)^2/F(z)$ is made. Extrapolation of the curve gives $1/\Lambda^0$ as intercept from which a new value of Λ^0 may be determined. This process is repeated until the value of Λ^0 remains constant. The slope of the final plot is $1/K(\Lambda^0)^2$.

An alternate method for the determination of K is that of Shedlovsky. He defines the degree of dissociation as:

$$\alpha = \frac{\Lambda S(z)}{\Lambda^0} \qquad (9)$$

where z is obtained by equation (5) and S(z) is given by:

$$S(z) = 1 + z + \frac{z^2}{2} + \cdots\cdots \qquad (10)$$

Using these relations we obtain

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda^0} + \frac{c\,\Lambda (y\pm)^2 S(z)}{K(\Lambda^0)^2} \qquad (11)$$

which is used in the same manner as is the Fuoss equation.

The data for both methods are recorded in Tables VIII-XV and the graphs of the respective approximations are shown in figures 2-11.

Computations pertaining to the 80% dioxane solutions were abandoned due to the fact that the exceptionally low values of Λ rendered the determination of F(z) and S(z) impossible. Also, it may be noticed that data pertaining to concentrations less than 9×10^{-5} were excluded from all but the first approximations. This was done because of the complexities they produced in the curves and because eliminating them showed no apparent effect upon the final results.

Both of the previously mentioned methods were used in the computation of data for the first approximation for each solvent. No differences

in the natures of the resulting curves were noticed and since the intercepts were the same, it was decided to use Shedlovsky's method for subsequent computations as it is less time consuming.

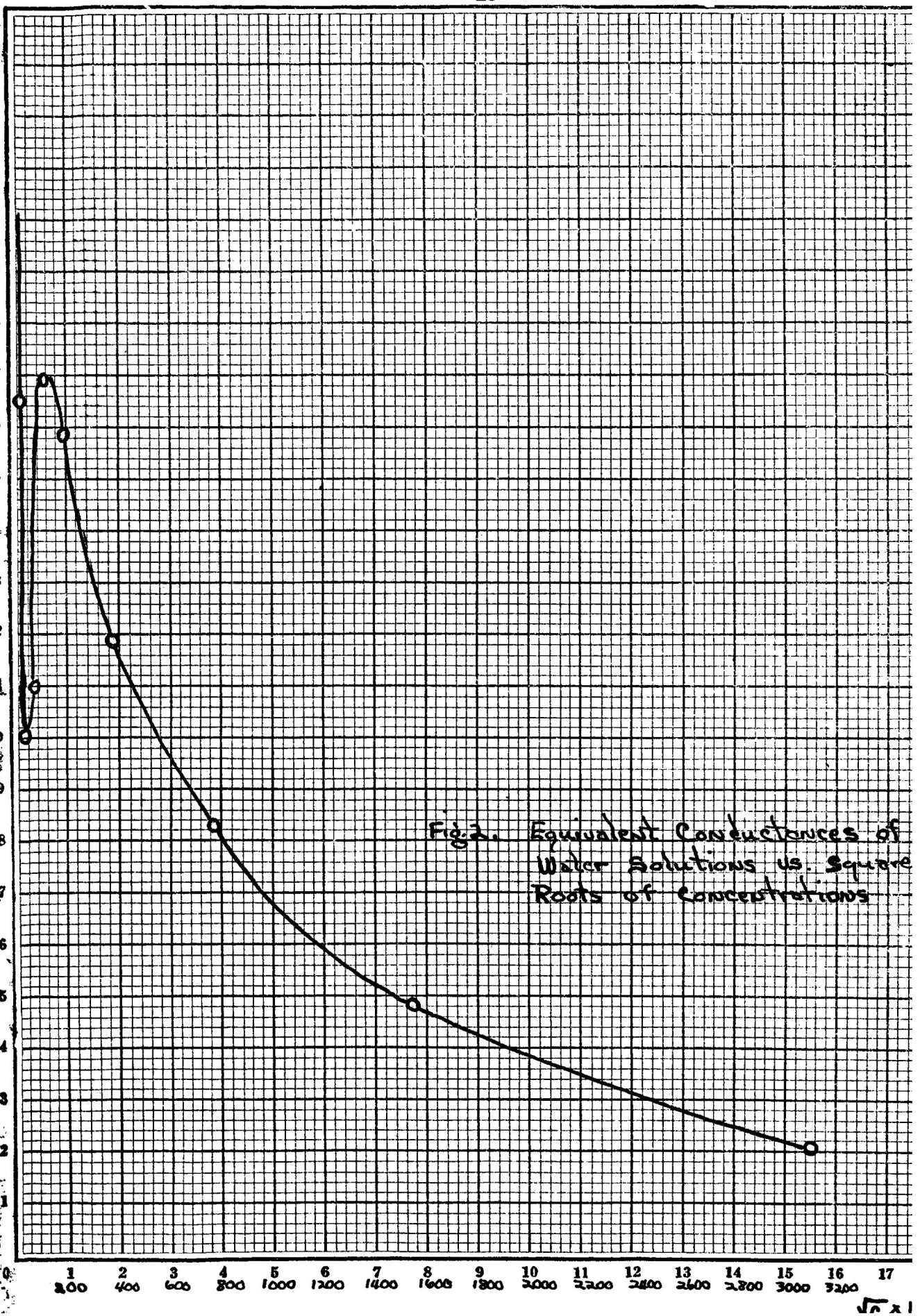

Fig. 2. Equivalent Conductances of Water Solutions vs. Square Roots of Concentrations

TABLE VIII

DATA FOR FIRST CORRECTED APPROXIMATION IN THE DETERMINATION OF THE LIMITING CONDUCTANCE OF WATER SOLUTIONS

$C \times 10^5$	R	R Corrected	Λ	Λ°	S_Λ	z	$F(z)$	$S(z)$	α Fuoss	α Shed.	$y^\pm$ Fuoss	$y^\pm$ Shed.	$\frac{1}{\Lambda S(z)} \times 10^5$	$C\Lambda(y^\pm)^2 S \times 10^2$
9600	10.00	10.00	42.29	388	148.37	.03912	.96015	1.0406	.1135	.1134	1.1296	1.1294	2272.4	533.85
2400	17.61	17.61	96.030			.02947	.97004	1.0299	.2442	.2609	1.0956	1.0967	1010.7	283.50
600.0	40.83	40.87	165.57			.01935	.98041	1.0195	.4353	.4351	1.0615	1.0614	592.37	113.85
150.0	114.35	114.62	236.14			.01155	.98837	1.0116	.6158	.6157	1.0361	1.0361	418.62	38.434
37.50	339.90	342.37	316.25			.00668	.99332	1.0067	.8206	.8205	1.0207	1.0206	314.10	12.434
9.400	1246.8	1280	337.44			.00346	.99653	1.0035	.8728	.8727	1.0106	1.0106	295.30	3.251
2.300	6896	8058	219.06			.00139	.99861	1.0014	.5712	.5698	1.0042	1.0042		
.5800	20252	35088	199.52			.00066	.99934	1.0007	.5145	.5138	1.0020	1.0020		
.1450	30644	85470	327.61			.00042	.99958	1.0004	.8447	.8440	1.0013	1.0013		

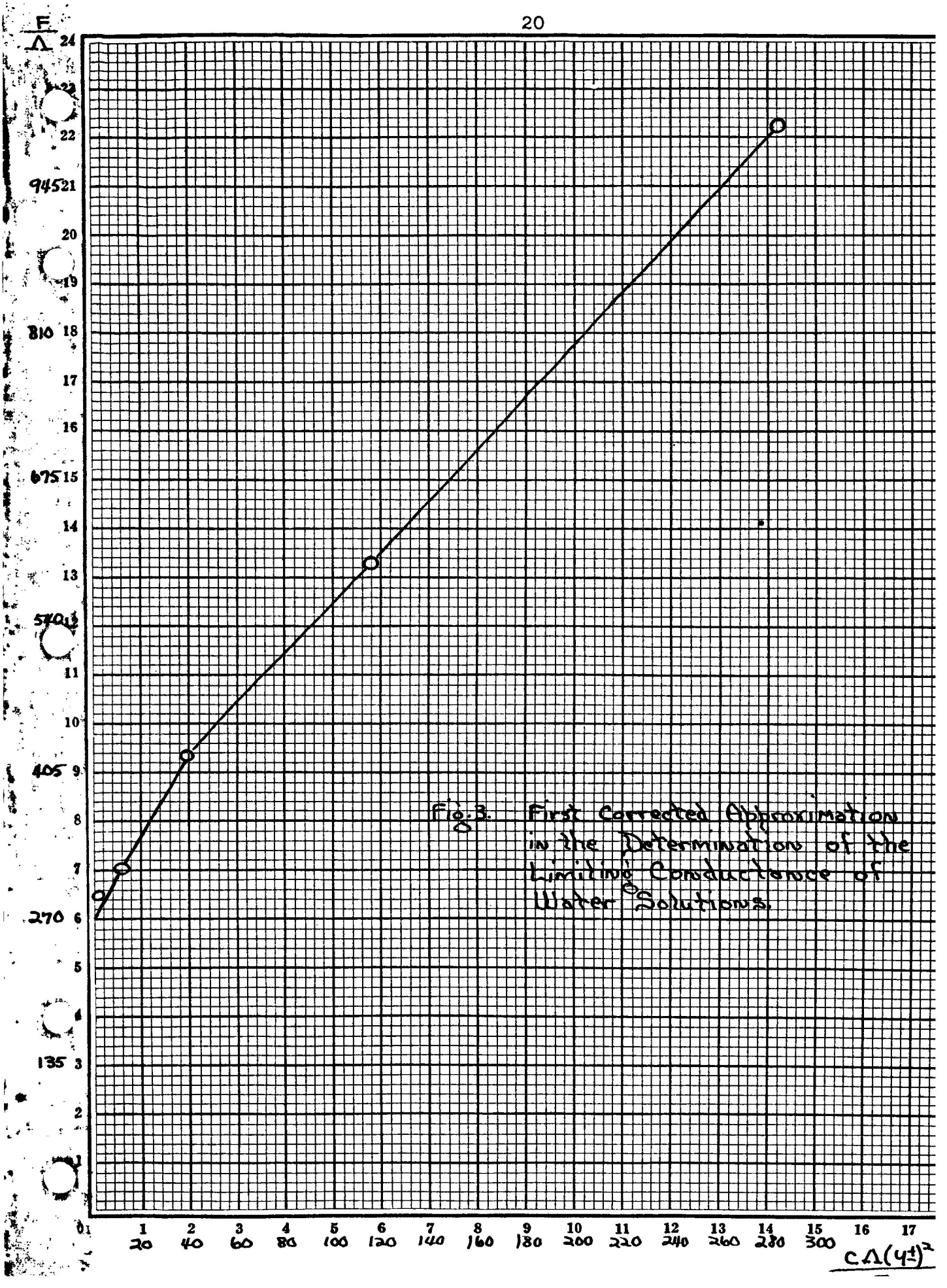

Fig. 3. First Corrected Approximation in the Determination of the Limiting Conductance of Water Solutions.

TABLE IX

DATA FOR SECOND CORRECTED APPROXIMATION IN THE DETERMINATION OF THE LIMITING CONDUCTANCE OF WATER SOLUTIONS

$C \times 10^5$	Λ	Λ°	S_Λ	z	$S(z)$	α	$y^\pm$	$\frac{1}{\Lambda S(z)} \times 10^5$	$C\Lambda(y^\pm)^2 S \times 10^2$
9600	53.240	377.5	145.98	.03574	1.0364	0.1149	1.1304	2304.2	528.95
2400	96.064			.02693	1.0273	0.2613	1.0969	1013.7	290.04
600	165.68			.01768	1.0180	0.4461	1.0623	593.24	113.86
150	236.14			.01056	1.0107	0.6322	1.0366	419.0	38.43
37.5	316.25			.00611	1.0061	0.8429	1.0210	314.3	12.43
9.4	337.44			.00316	1.0032	0.8967	1.0108	295.4	3.251

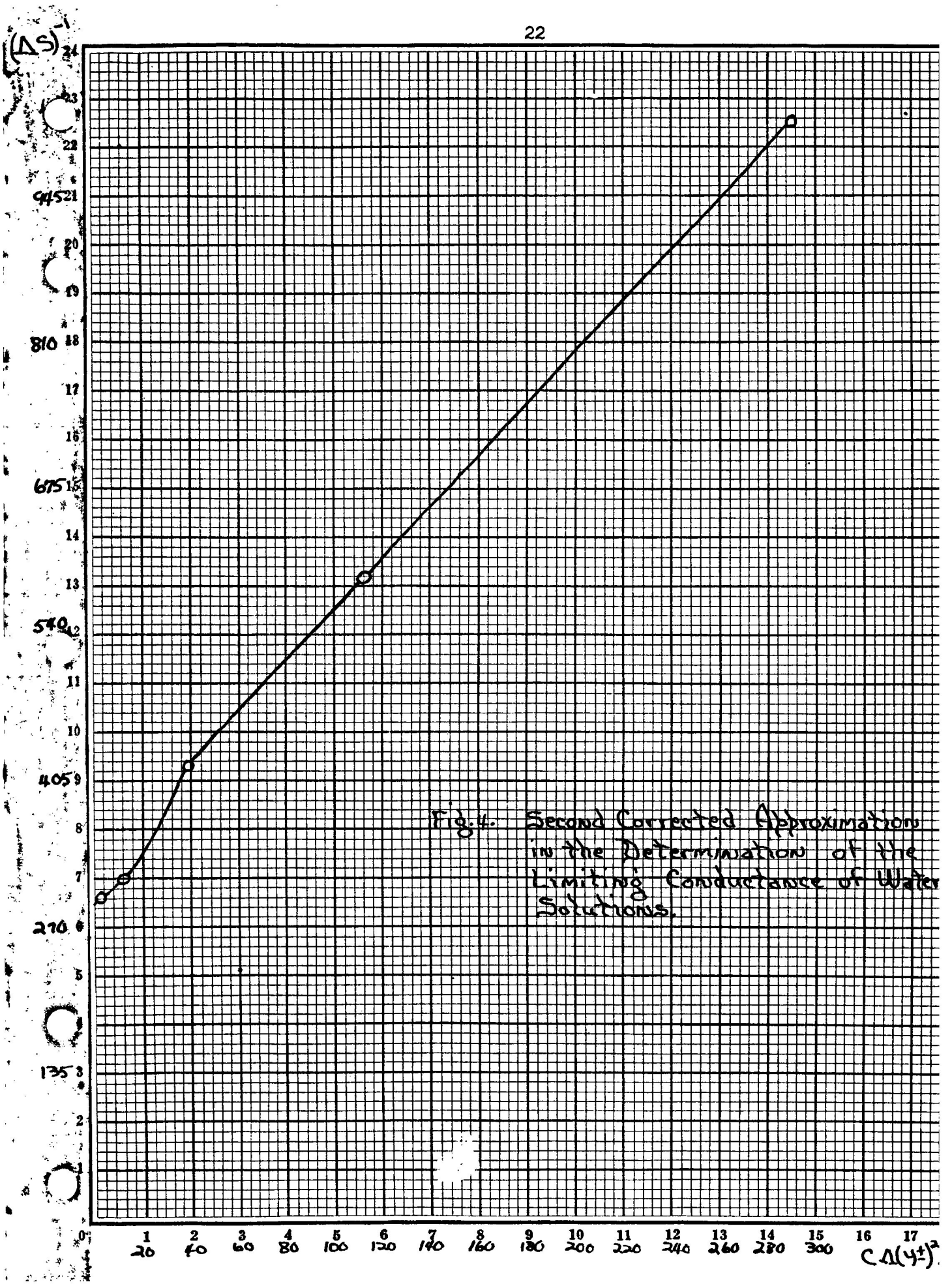

Fig. 4. Second Corrected Approximation in the Determination of the Limiting Conductance of Water Solutions.

TABLE X

DATA FOR THIRD CORRECTED APPROXIMATION IN THE DETERMINATION OF THE LIMITING CONDUCTANCE OF WATER SOLUTIONS

$c \times 10^5$	Λ	Λ°	S_Λ	z	$S(z)$	α	$y^\pm$	$\frac{1}{\Lambda S(z)} \times 10^5$	$c\Lambda(y^\pm)^2 S \times 10^2$
9600	53.240	343.6	138.26	.04274	1.0437	.1285	1.1384	2265.6	549.06
2400	96.064			.03220	1.0337	.2889	1.1020	1007.7	289.34
600	165.68			.02114	1.0214	.4922	1.0654	591.30	115.20
150	236.14			.01262	1.0126	.6959	1.0384	418.15	38.679
37.5	316.25			.007474	1.0075	.9272	1.0220	313.80	12.195
9.4	337.44			.004756	1.00476	.9857	1.0142	294.90	3.2755

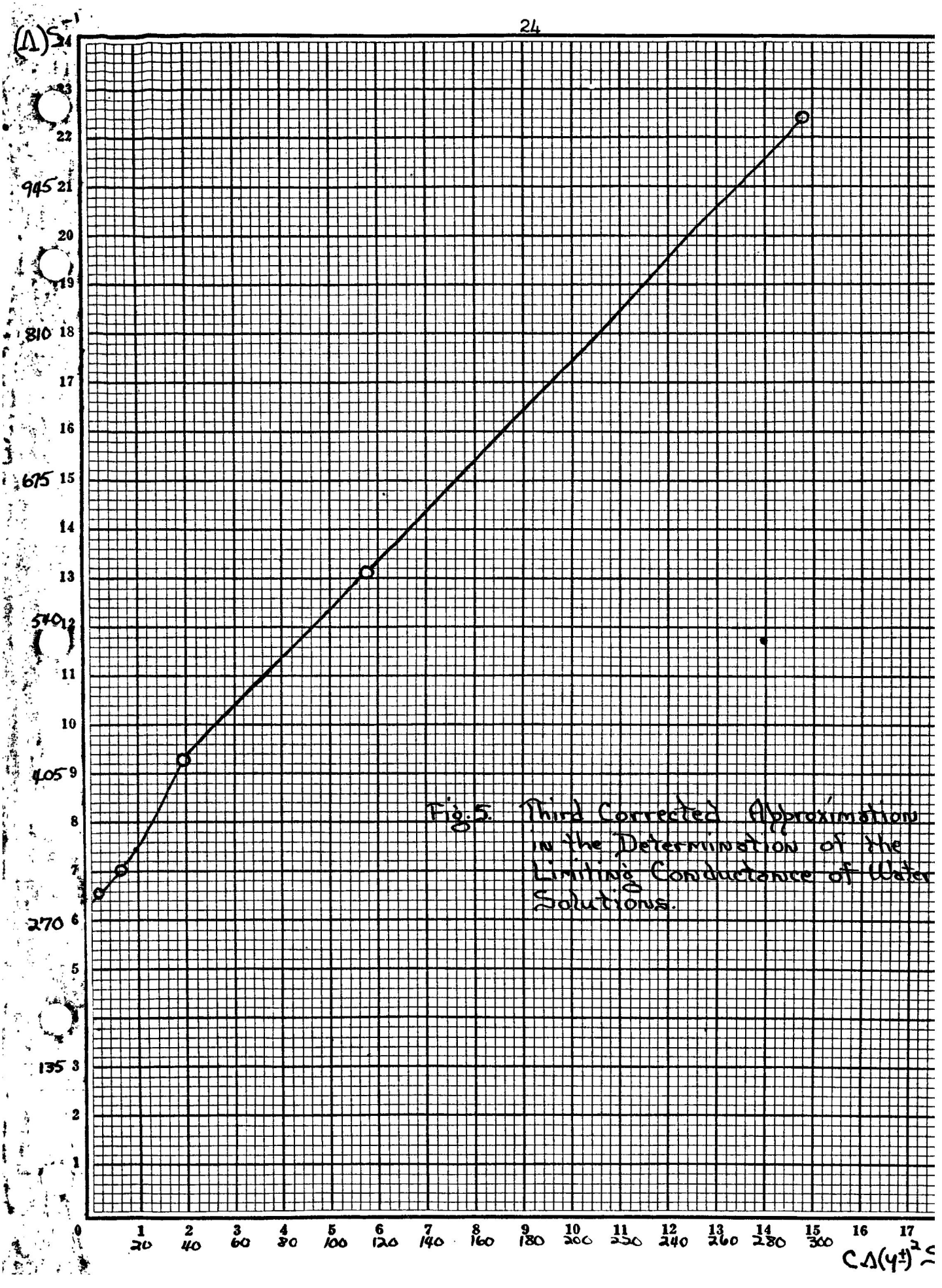

Fig. 5. Third Corrected Approximation in the Determination of the Limiting Conductance of Water Solutions.

TABLE XI

DATA FOR FOURTH CORRECTED APPROXIMATION IN THE DETERMINATION OF THE LIMITING CONDUCTANCE OF WATER SOLUTIONS

$C \times 10^5$	Λ	Λ°	S_Λ	z	$S(z)$	α	$\gamma^\pm$	$\frac{1}{\Lambda S(z)} \times 10^5$	$C\Lambda(\gamma^\pm)^2 S \times 10^2$
9600	53.240	350.26	139.77	.04296	1.0438	.11541	1.1307	2265.3	541.80
2400	96.064			.03232	1.03284	.26502	1.0975	1008.3	293.40
600	165.68			.02171	1.02193	.46185	1.0634	591.00	114.79
150	236.14			.01267	1.01275	.66460	1.0375	418.17	38.61
37.5	316.25			.00733	1.00733	.89490	1.0216	313.92	12.18
9.4	337.44			.00379	1.00379	.9582	1.0111	295.23	3.26

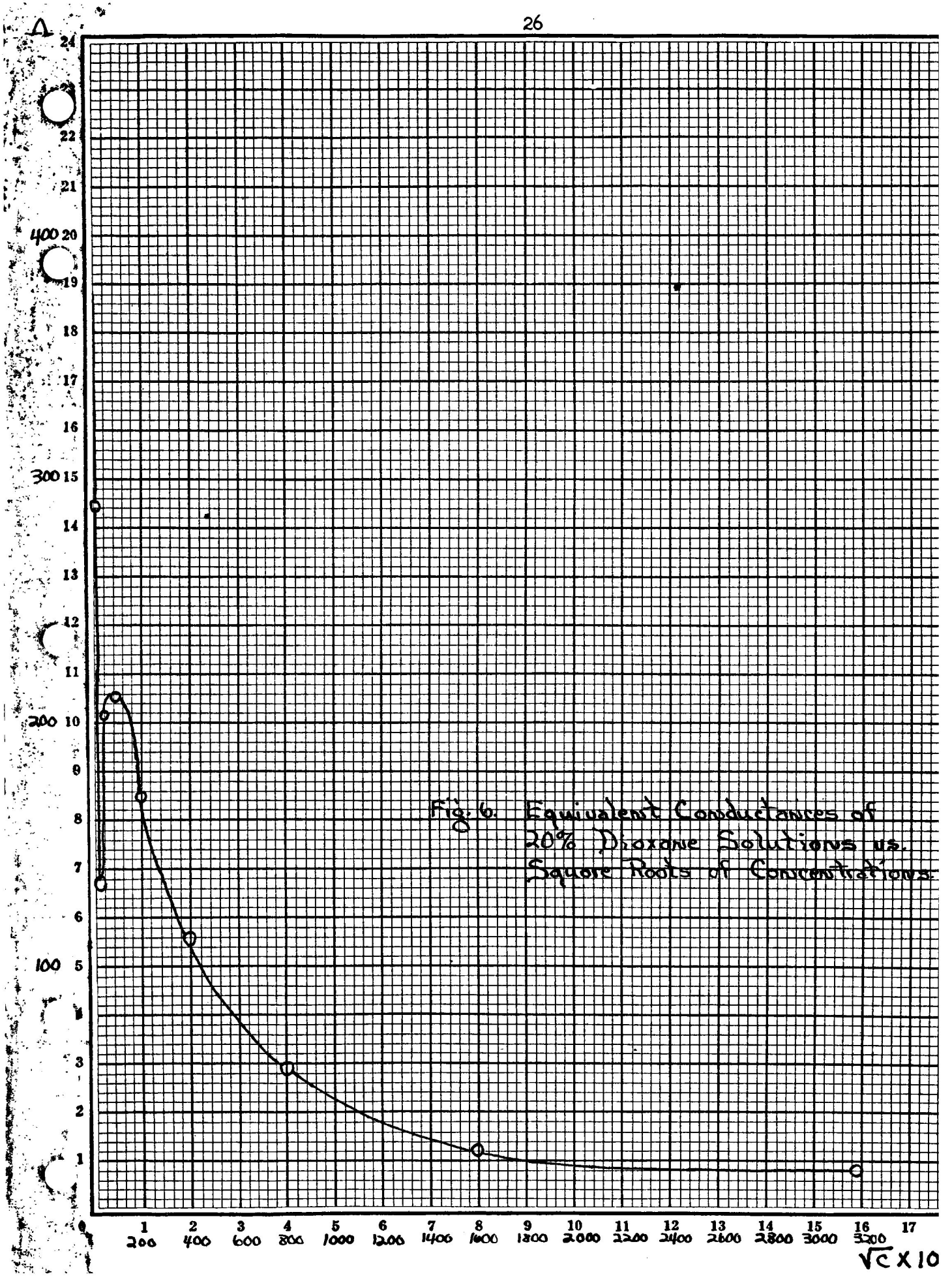

Fig. 6: Equivalent Conductances of 20% Dioxane Solutions vs. Square Roots of Concentrations.

TABLE XII

DATA FOR FIRST CORRECTED APPROXIMATION IN THE DETERMINATION OF THE LIMITING CONDUCTANCE OF 20 PER CENT DIOXANE SOLUTIONS.

$C \times 10^5$	R	R corrected	Λ	Λ°	S_Λ	z	F(z)	S(z)	α Fuoss	α Shed.	$\gamma\pm$ Fuoss	$\gamma\pm$ Shed.	$\frac{10^5}{\Lambda S(z)}$	$C\Lambda(\gamma\pm)^2 S \times 10^3$
10,000	25.75	25.76	15.60	364	168.86	0.03052	0.96899	1.0310	0.04223	0.04408	1.1213	1.1210	601.60	2041.5
2530	64.50	64.58	24.85			.01928	0.98048	1.0195	0.06963	0.06957	1.0745	1.0745	394.90	739.65
632	111.2	111.4	57.66			.01469	0.98516	1.01074	0.1608	0.1601	1.0560	1.0560	171.60	410.66
158	229.1	230.0	111.7			.00811	0.99187	1.0082	0.3094	0.3093	1.0386	1.0386	88.81	191.90
39.5	595.2	601.7	170.8			.00632	0.99358	1.00634	0.4723	0.4721	1.0236	1.0236	58.19	71.131
9.88	1889	1956	210.1			..00351	0.99749	1.00351	0.5793	0.5793	1.0130	1.0130	47.30	21.379
2.47	7069	8078	203.5			.00173	0.99826	1.00173	0.5600	0.5581	1.0064	1.0064		
.618	25960	4873	134.8			.00070	0.99930	1.00070	0.3706	0.3701	1.0030	1.0030		
.155	34230	8921	293.6			.00052	0.99948	1.00052	0.8071	0.8063	1.0018	1.0018		

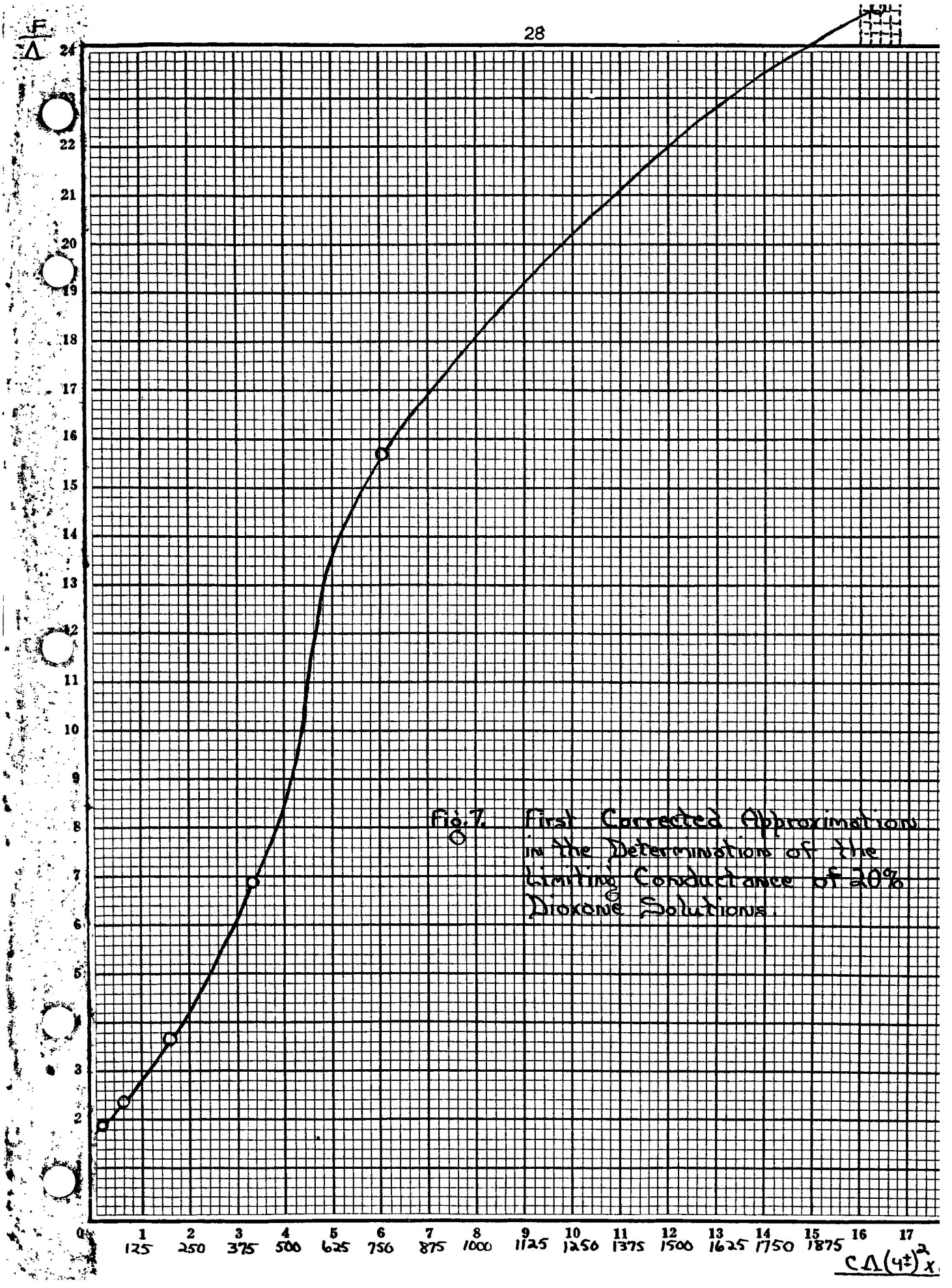

Fig. 7. First Corrected Approximation in the Determination of the Limiting Conductance of 20% Dioxane Solutions.

TABLE XIII

DATA FOR SECOND CORRECTED APPROXIMATION IN THE DETERMINATION OF THE LIMITING CONDUCTANCE OF 20 PER CENT DIOXANE SOLUTIONS

$C \times 10^5$	Λ	Λ°	S_Λ	z	$S(z)$	α	$\gamma^\pm$	$\frac{1}{\Lambda S(z)} \times 10^5$	$C\Lambda(\gamma^\pm)^2 S \times 10^3$
10,100.	15.60	238.1	126.76	.04351	1.0444	.06843	1.1530	613.87	2187.5
2530	24.85			.02736	1.0281	.1073	1.0933	391.40	772.67
632	57.66			.02083	1.0210	.2472	1.0700	169.93	425.97
158	111.7			.01449	1.0146	.4770	1.0483	88.230	196.79
39.5	170.8			.00896	1.0090	.7408	1.0297	58.016	72.190
9.88	210.1			.00497	1.0050	.8889	1.0162	47.360	21.543

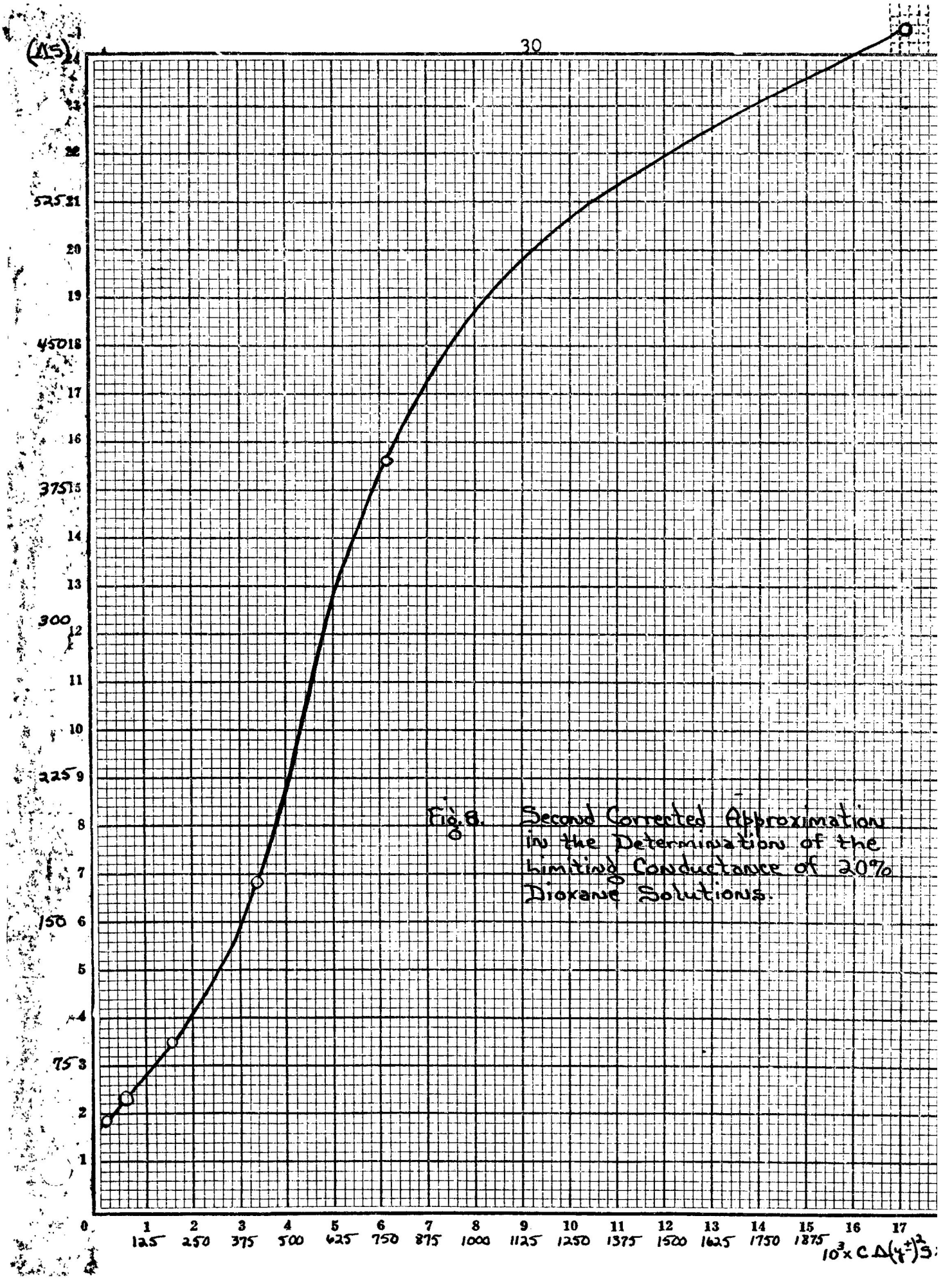

Fig. 8. Second Corrected Approximation in the Determination of the Limiting Conductance of 20% Dioxane Solutions.

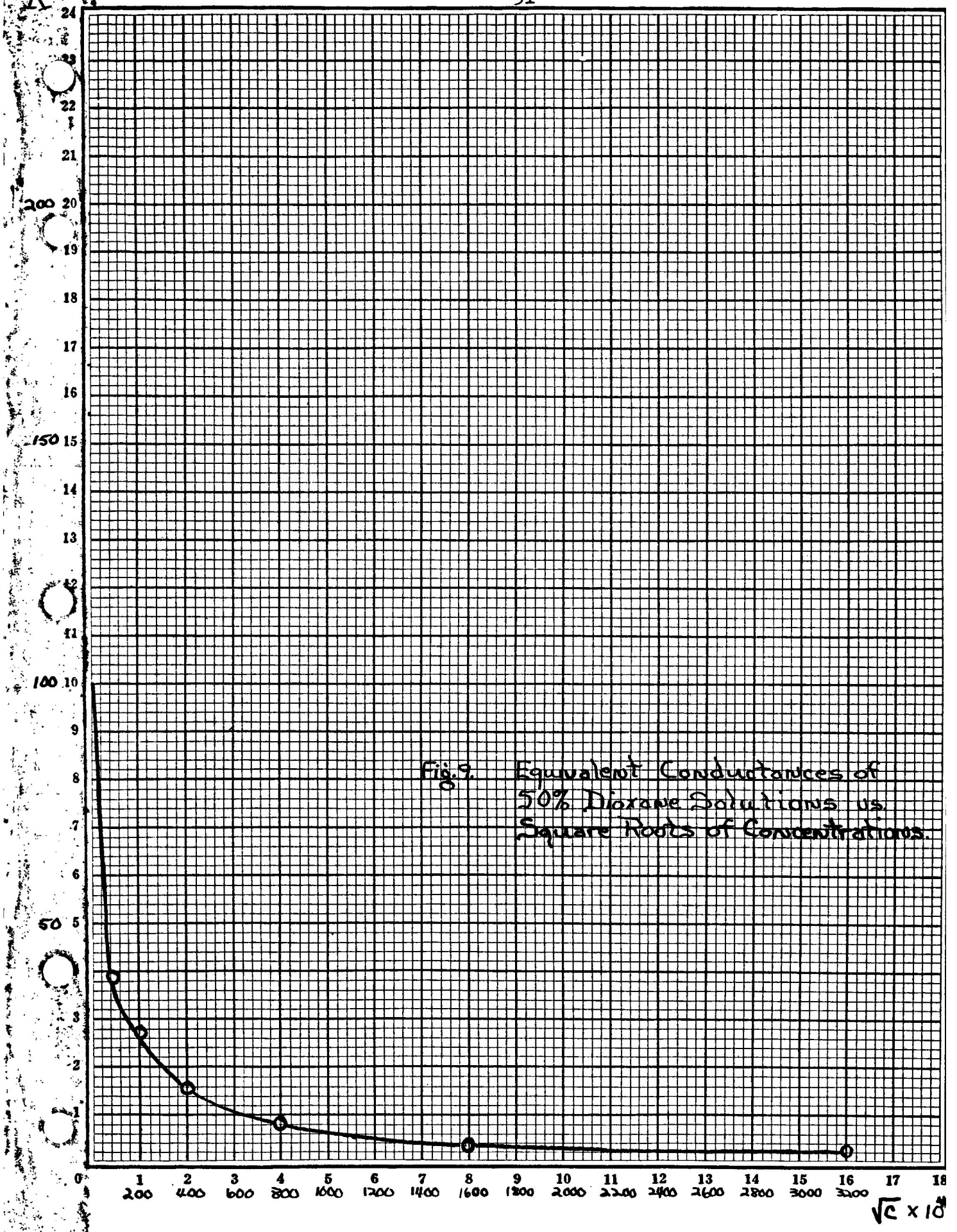

Fig. 9. Equivalent Conductances of 50% Dioxane Solutions vs. Square Roots of Concentrations.

TABLE XIV

DATA FOR FIRST CORRECTED APPROXIMATION IN THE DETERMINATION OF THE LIMITING CONDUCTANCE OF 50 PER CENT DIOXANE SOLUTIONS

$C \times 10^5$	R	R Corrected	Δ	Δ°	S_Δ	z	$F(z)$	$S(z)$	α Fuoss	α shed.	$y^\pm$ Fuoss	$y^\pm$ shed.	$C\Delta(y^\pm)^2 S \times 10^3$	$\frac{1}{\Delta S} \times 10^3$
10.300	168.2	168.4	2.34	210	207.77	.03352	.96587	1.0342	.01154	.01153	1.0093	1.0092	253.92	413.2
2580	371.8	371.9	4.23			.02256	.97716	1.0228	.02062	.02061	1.0061	1.0061	113.04	231.1
645	771.2	777.0	8.10			.01561	.98423	1.0157	.03920	.03917	1.0042	1.0043	53.512	121.6
161	1646	1672	15.09			.01064	.98930	1.0107	.07258	.07257	1.0029	1.0029	24.678	65.62
40	3650	3783	26.83			.00707	.99293	1.0071	.1286	.1286	1.0020	1.0019	10.847	37.02
10	9571	10550	38.49			.00424	.99576	1.0043	.1841	.1841	1.0011	1.0012	3.8743	25.87

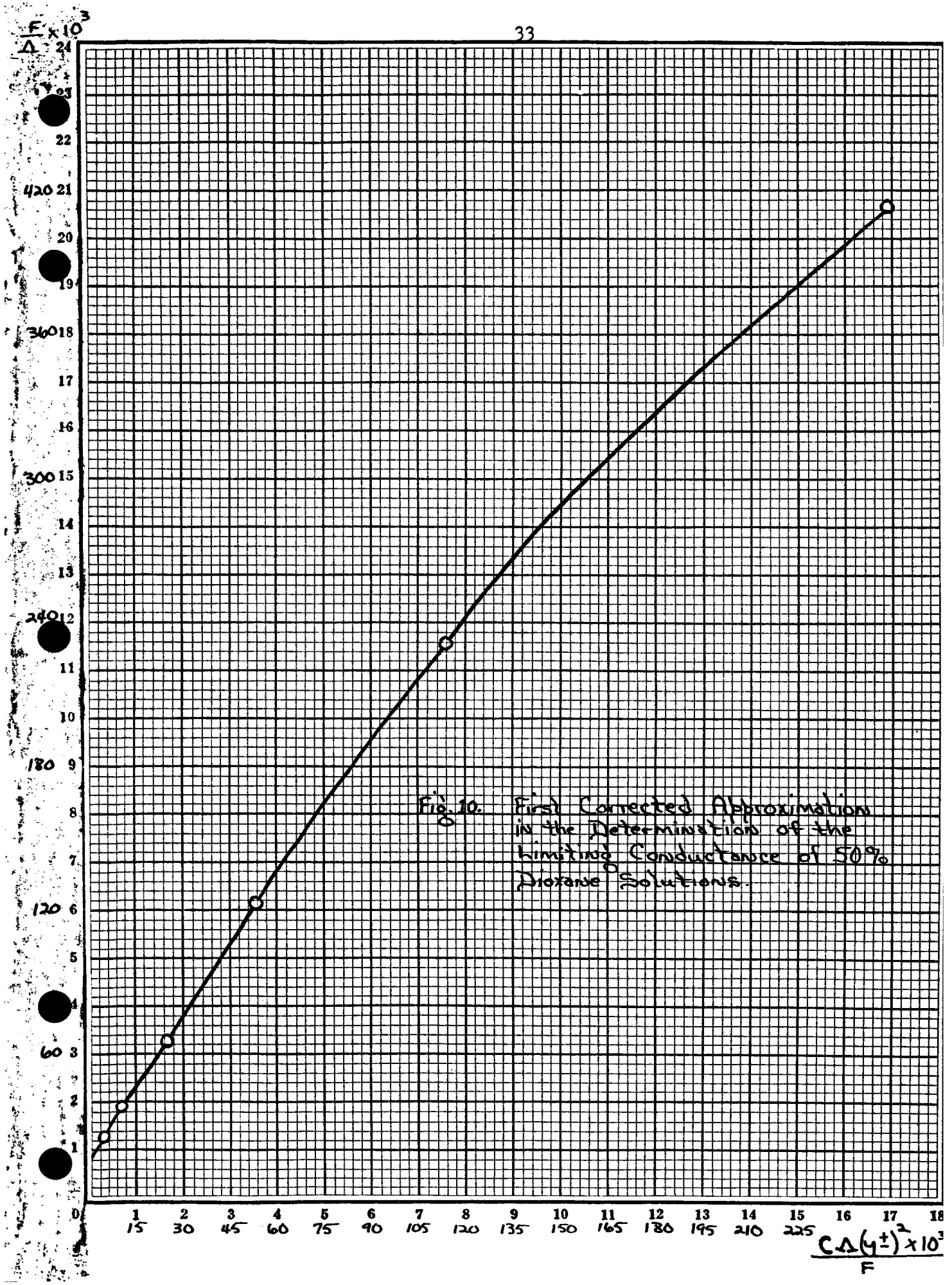

Fig. 10. First Corrected Approximation in the Determination of the Limiting Conductance of 50% Dioxane Solutions.

TABLE XV

DATA FOR SECOND CORRECTED APPROXIMATION IN THE DETERMINATION OF THE LIMITING CONDUCTANCE OF 50 PER CENT DIOXANE SOLUTIONS

$C \times 10^5$	Λ	Λ°	S_Λ	z	$S(z)$	α	$\gamma^{\pm}$	$\frac{1}{\Lambda S(z)} \times 10^3$	$C\Lambda(\gamma^{\pm})^2 S \times 10^3$
10.300	2.34	58.82	88.488	.09631	1.1056	0.04399	1.0181	386.47	276.26
2580	4.23			.06481	1.0669	0.07675	1.0120	221.51	119.33
645	8.10			.04484	1.0458	0.1440	1.0065	118.03	55.36
161	15.09			.03056	1.0310	0.22643	1.0055	64.33	25.31
40	26.83			.02032	1.0205	0.4654	1.0036	36.53	11.03
10	38.49			.01217	1.0122	0.6623	1.0027	25.67	3.91

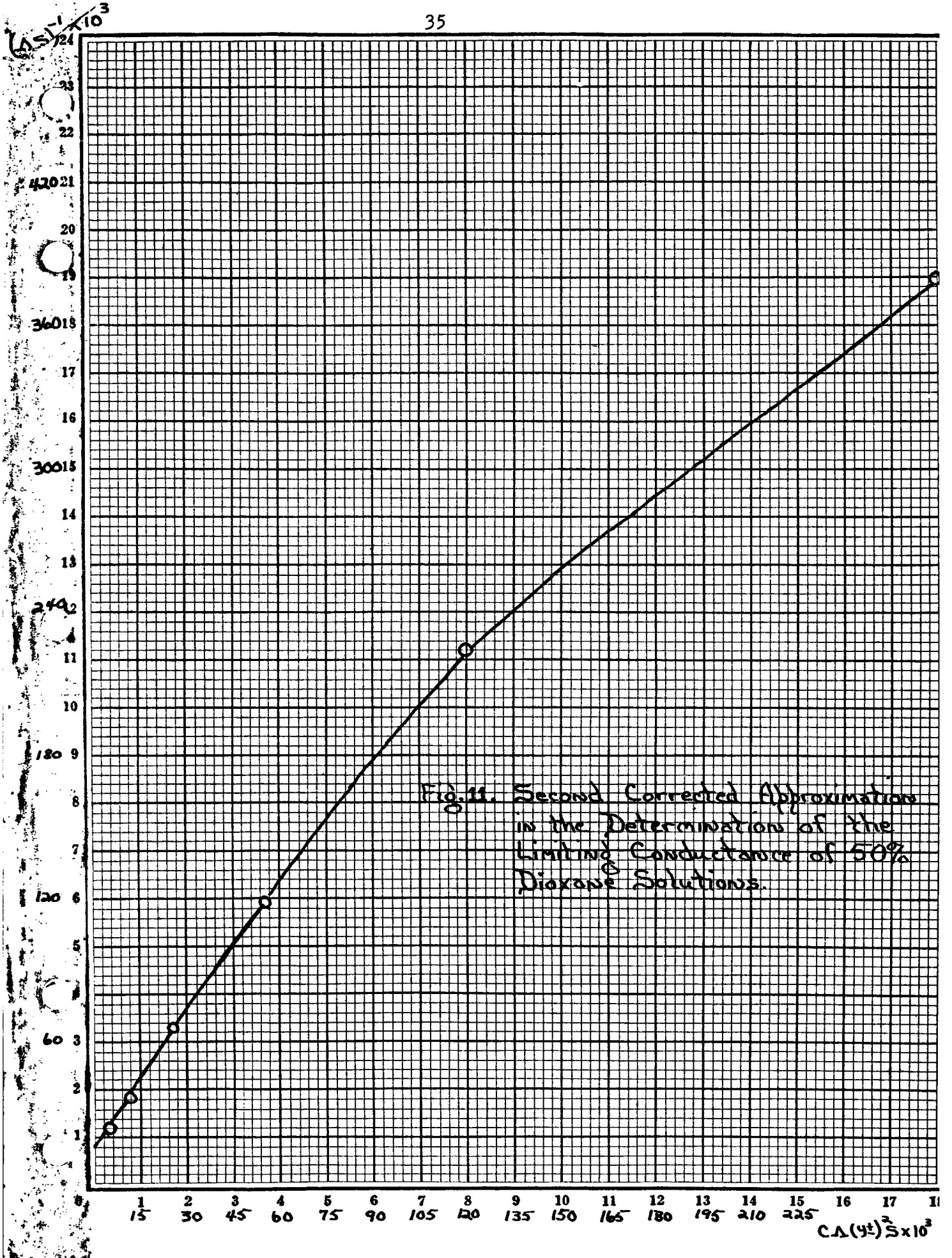

Fig. 11. Second Corrected Approximations in the Determination of the Limiting Conductance of 50% Dioxane Solutions.

The slopes and intercepts were determined by the method of averages.[35] These values and the corresponding dissociation constants are shown in Table XVI.

TABLE XVI

CALCULATED SLOPES, INTERCEPTS AND DISSOCIATION CONSTANTS

Solution	Intercept x 10^3		Slope x 10^3	K x 10^3
50% Dioxane	17.51	57.13	1828	.1677
20% Dioxane	4.244	235.7	22.85	7.879
Water	2.855	350.3	3.155	2.584

The value obtained for the limiting conductance of chloroacetic acid in water is considerably lower than the literature value of 388.5, at 25° C. and, as is to be expected, the value of the dissociation constant is higher than the literature value[36] (1.396×10^{-3}). It is believed that the discrepancy is due to the fact that measured resistances are invariably high due to frequency effects and our data was of such a nature that it could not be corrected for such effects.

We found no evidence of triple-ion formation which is in agreement with Kraus, that triple-ions form in media of dielectric constants below 10. We were unable to measure resistances in such media. It was noticed that resistances of solutions at the lower concentrations increased with time, and it was assumed that this was due to prior adsorption of ions either by the electrodes or by the glass. The effects of this is noticed in the character of the plots at the lower concentrations. (Figures II and III). No attempt was made in this work to correct for such effects.

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[35] F. Daniels, "Mathematical Preparation for Physical Chemistry," McGraw-Hill Book Co., Inc., New York, 1928, p. 235.

[36] B. S. Saxton and T. W. Langer, J. Am. Chem. Soc., 55, 3638 (1933).

SUMMARY

1. Resistances of monochloroacetic acid in several solvents have been measured at 25° C. using bright electrodes, and the respective dissociation constants determined.

2. High values of dissociation constants are to be expected when computed from conductance data unless correction is made for frequency effects.

3. For precise results in the measurement of resistances of solutions, correction should be made for adsorption of ions in the conductance cell.

4. Complex-ion formation is not to be found in solutions of dielectric constant greater than 30.

5. The methods of Fuoss and of Shedlovsky are compared.

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